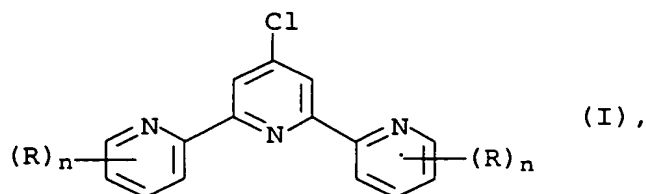


We claim:

1. A process for preparing terpyridines of the formula I



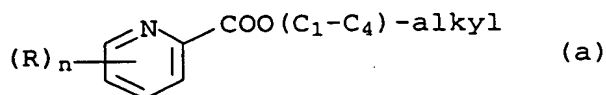
in which

R are hydrogens or identical C₁-C₁₂-alkyl or C₁-C₁₂-alkoxy radicals and

n is 0, 1, 2, 3 or 4 and is the same for both sets of radicals R,

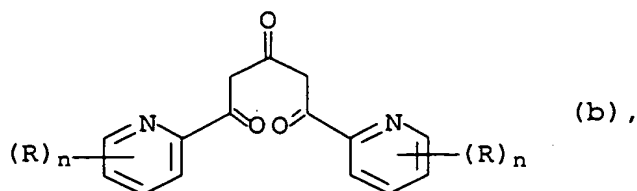
by successive reaction steps comprising

- A) condensation of a C₁-C₄-alkyl pyridine-2-carboxylate derivative of the formula a



30 with acetone in an aprotic solvent in the presence of a base,

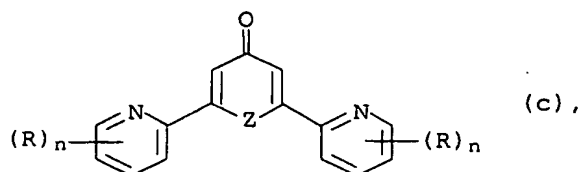
- B) reaction of the 1,5-bis(2-pyridyl)pentane-1,3,5-trione derivative of the formula b



45

obtained in reaction step A with ammonia or ammonium salts $(\text{NH}_4)_q\text{Y}$ with removal of the water of reaction formed, where the variable Y in $(\text{NH}_4)_q\text{Y}$ is the anion of the parent q-basic acid H_qY of the ammonium salt, and

- C) chlorination of the 2,6-bis(2-pyridyl)-4(1H)pyridinone derivative of the formula c obtained in reaction step B,

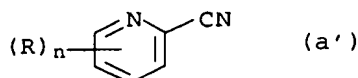


where Z is NH in the case of a reaction with ammonia in reaction step B and is $\text{NH}_2^{\oplus}[\text{Y}_{1/q}]^{\ominus}$ in the case of a reaction with ammonium salt $(\text{NH}_4)_q\text{Y}$ in reaction step B,

wherein

the reaction step A is preceded by a reaction step A' in which the $\text{C}_1\text{-C}_4$ -alkyl pyridine-2-carboxylate derivative of the formula a is obtained by

- A') acid hydrolysis of a 2-cyanopyridine derivative of the formula a'



by means of an anhydrous inorganic acid or its anhydride in the presence of water and a $\text{C}_1\text{-C}_4$ -alkanol, with an equimolar amount of water being added to the 2-cyanopyridine derivative of the formula a' prior to addition of the anhydrous inorganic acid or its anhydride,

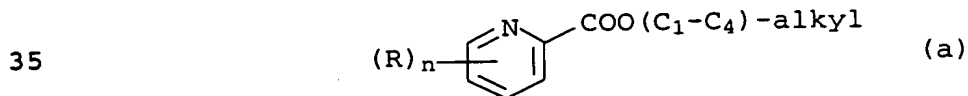
the base used in reaction step A is an alkali metal $\text{C}_1\text{-C}_4$ -alkoxide or alkaline earth metal $\text{C}_1\text{-C}_4$ -alkoxide,

the removal of the water of reaction in reaction step B is carried out using a $\text{C}_1\text{-C}_4$ -alkanol as entrainer

and

the chlorination of the 2,6-bis(2-pyridyl)-4(1H)pyridinone derivative of the formula c in reaction step C is carried out using phosphorus oxide chloride (POCl₃) or using a mixture comprising phosphorus oxide chloride and at least one organic solvent selected from the group consisting of toluene, o-xylene, m-xylene and p-xylene.

2. A process as claimed in claim 1, wherein the base used in reaction step A is an alkali metal C₁-C₄-alkoxide.
3. A process as claimed in claim 1, wherein the base used in reaction step A is sodium C₁-C₄-alkoxide.
4. A process as claimed in claim 1, wherein the base used in reaction step A is sodium ethoxide.
5. A process as claimed in claim 1, wherein the removal of the water of reaction in reaction step B is carried out using ethanol, n-propanol, i-propanol or n-butanol as entrainer.
6. A process as claimed in claim 1, wherein the removal of the water of reaction in reaction step B is carried out using ethanol as entrainer.
7. A process as claimed in claim 1, wherein the chlorination of the 2,6-bis(2-pyridyl)-4(1H)pyridinone derivative of the formula b is carried out using phosphorus oxide chloride (POCl₃) or using a mixture comprising phosphorus oxide chloride and toluene.
8. A process for preparing C₁-C₄-alkyl pyridine-2-carboxylate derivatives of the formula a

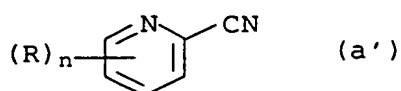


in which

- R is hydrogen or a C₁-C₁₂-alkyl or C₁-C₁₂-alkox radical and
- n is 0, 1, 2, 3 or 4,

by acid hydrolysis of a 2-cyanopyridine derivative of the formula a'

26

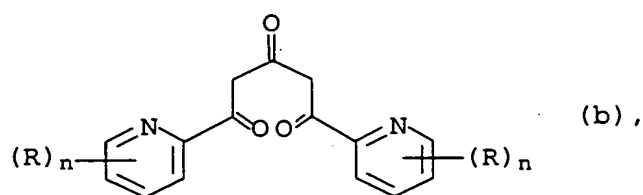


5 by means of an anhydrous inorganic acid or its anhydride in the presence of water and a C₁-C₄-alkanol, wherein an equimolar amount of water is added to the 2-cyanopyridine derivative of the formula a' prior to addition of the anhydrous inorganic acid or its anhydride.

10

9. A process for preparing 1,5-bis(2-pyridyl)pentane-1,3,5-trione derivatives of the formula b

15



20

in which

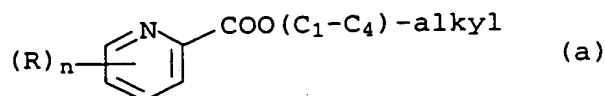
R are hydrogens or identical C₁-C₁₂-alkyl or C₁-C₁₂-alkoxy radicals and

25

n is 0, 1, 2, 3 or 4 and is the same for both sets of radicals R,

30

by condensation of the C₁-C₄-alkyl pyridine-2-carboxylate derivative of the formula a



35

with acetone in an aprotic solvent in the presence of an alkali metal C₁-C₄-alkoxide or alkaline earth metal C₁-C₄-alkoxide as base.

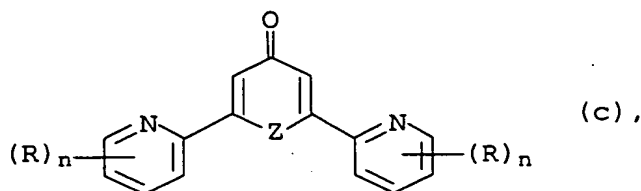
- 40 10. A process as claimed in claim 9, wherein the base used is an alkali metal C₁-C₄-alkoxide.

11. A process as claimed in claim 9, wherein the base used is sodium C₁-C₄-alkoxide.

45

12. A process as claimed in claim 9, wherein the base used is sodium methoxide.

13. A process for preparing 2,6-bis(2-pyridyl)-4(1H)pyridinone derivatives of the formula c



in which

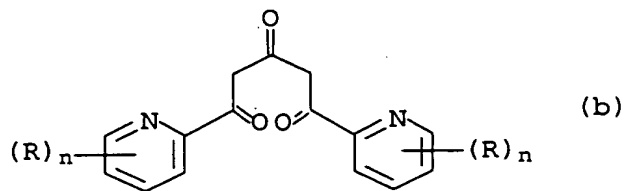
R are hydrogens or identical C₁-C₁₂-alkyl or C₁-C₁₂-alkoxy radicals,

n is 0, 1, 2, 3 or 4 and is the same for both sets of radicals R,

Z is NH or NH₂[⊕][Y_{1/q}][⊖] and

Y is the anion of a q-basic acid H_qY,

by reacting the 1,5-bis(2-pyridyl)pentane-1,3,5-trione derivative of the formula b

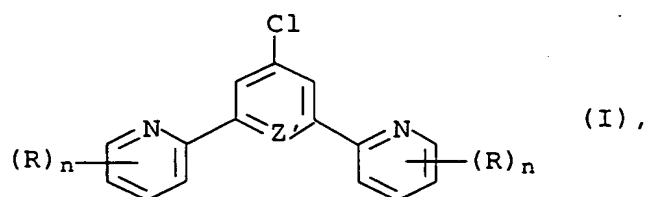


with ammonia or ammonium salts (NH₄)_qY with removal of the water of reaction formed, wherein the removal of the water of reaction is carried out using a C₁-C₄-alkanol as entrainer.

14. A process as claimed in claim 13, wherein the removal of the water of reaction is carried out using ethanol, n-propanol, i-propanol or n-butanol as entrainer.

15. A process as claimed in claim 13, wherein the removal of the water of reaction is carried out using ethanol as entrainer.

16. A process for preparing terpyridines of the formula I



10 in which

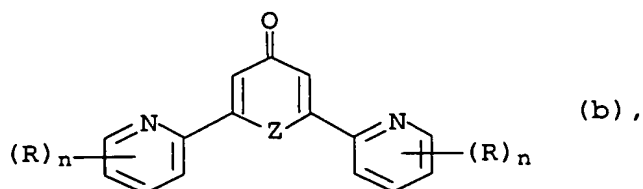
R are hydrogens or identical C₁-C₁₂-alkyl or C₁-C₁₂-alkoxy radicals,

15 n is 0, 1, 2, 3 or 4 and is the same for both sets of radicals R,

20 Z' is nitrogen or NH[⊕][Y_{1/q}][⊖] and

Y is the acid anion of a q-basic acid H_qY,

by chlorination of the 2,6-bis(2-pyridyl)-4(1H)pyridinone derivative of the formula b



where Z is NH or NH₂[⊕][Y_{1/q}][⊖],

35 wherein the chlorination is carried out using phosphorus oxide chloride (POCl₃) or using a mixture comprising phosphorus oxide chloride and at least one organic solvent selected from the group consisting of toluene, o-xylene, m-xylene and p-xylene.

40 17. A process as claimed in claim 16, wherein the chlorination is carried out using phosphorus oxide chloride (POCl₃) or using a mixture comprising phosphorus oxide chloride and toluene.

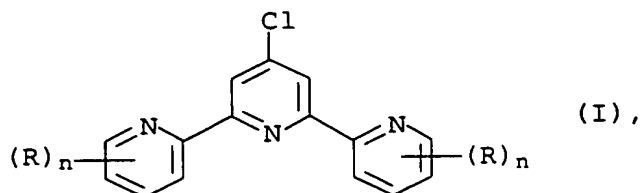
Preparation of terpyridines

Abstract

5

Process for preparing terpyridines of the formula I

10



15 in which

R are hydrogens or identical C_1 - C_{12} -alkyl or C_1 - C_{12} -alkoxy radicals and

20 n is 0, 1, 2, 3 or 4 and is the same for both sets of radicals R,

comprises the successive reaction steps:

25 A') acid hydrolysis of a 2-cyanopyridine derivative by means of an anhydrous inorganic acid or its anhydride in the presence of water and a C_1 - C_4 -alkanol, with an equimolar amount of water being added to the 2-cyanopyridine derivative prior to addition of the anhydrous inorganic acid or its anhydride,

30

A) condensation of the C_1 - C_4 -alkyl pyridine-2-carboxylate derivative obtained in reaction step A' with acetone in an aprotic solvent in the presence of an alkali metal C_1 - C_4 -alkoxide or alkaline earth metal C_1 - C_4 -alkoxide as base,

35

B) reaction of the 1,5-bis(2-pyridyl)pentane-1,3,5-trione derivative obtained in reaction step A with ammonia or ammonium salts $(NH_4)_qY$ with removal of the water of reaction formed using a C_1 - C_4 -alkanol as entrainer, where the variable Y in $(NH_4)_qY$ is the
40 anion of the parent q-basic acid H_qY of the ammonium salt, and

C) chlorination of the 2,6-bis(2-pyridyl)-4(1H)pyridinone derivative obtained in reaction step B using phosphorus oxide chloride ($POCl_3$) or using a mixture comprising phosphorus oxide
45 chloride and at least one organic solvent selected from the group consisting of toluene, o-xylene, m-xylene and p-xylene.

Also provided are a process for preparing C₁-C₄-alkyl pyridine-2-carboxylate derivatives from 2-cyanopyridine derivatives, a process for preparing 1,5-bis(2-pyridyl)pentane-1,3,5-trione derivatives by condensation of a C₁-C₄-alkyl
5 pyridine-2-carboxylate derivative with acetone, a process for preparing 2,6-bis(2-pyridyl)-4(1*H*)pyridinone derivatives by reaction of a 1,5-bis(2-pyridyl)pentane-1,3,5-trione derivative with ammonia or ammonium salts and a process for preparing terpyridines of the formula I by chlorination of a
10 2,6-bis(2-pyridyl)-4(1*H*)pyridinone derivative.

15

20

25

30

35

40

45